

PROCEEDINGS

**TWENTY-FIRST ASILOMAR CONFERENCE
ON
POLYMERIC MATERIALS**

February 22-25, 1998

SPONSORED BY

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SUBMITTED BY

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CONTENTS

- 1. Report Documentation Page**
- 2. Program**
- 3. Attendees**
- 4. Abstracts**

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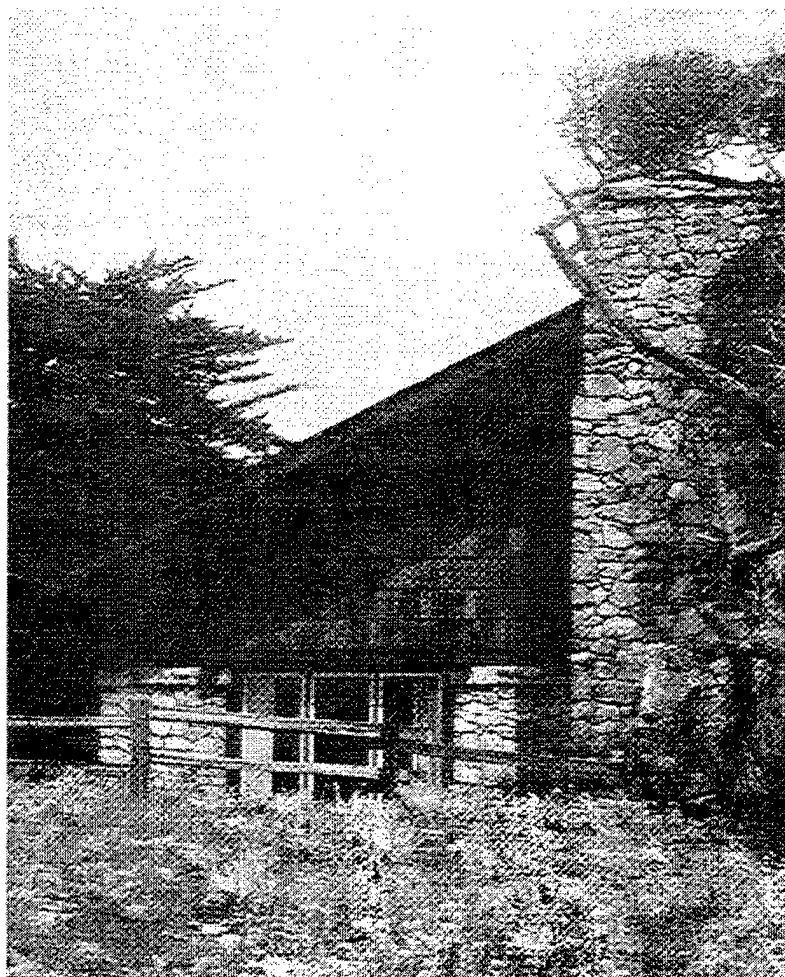
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13. ABSTRACT (Maximum 200 words) The 1998 Asilomar Conference on Polymeric Materials was devoted to interface/interphase design, control and property relationships. In particular, the conference focused on the development of new materials systems that are controlled by structure in interfacial regions at the nanoscale. Both synthetic polymeric materials and biological systems were considered. Special emphasis was on such issues as durability, property enhancement, compatibility, and integration with inorganic and biological compounds. As in previous years, this conference addressed the problems and opportunities that are arising with the emergence of a hierarchical approach in the design of new materials systems. This year, in particular, the conference focused on the newly emerging nano materials systems and the hierarchical approach interrelating our understanding of structure at various scales to solid state properties and materials processing. Such an approach may prove invaluable in the design of new polymers, their blends and composites, novel processing, and advanced materials systems in general.				
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Program

Asilomar Conference



***Twenty-First Asilomar Conference
on Polymeric Materials***

February 22-25, 1998

Pacific Grove, CA

***Twenty-First Asilomar Conference
on Polymeric Materials
February 22-25, 1998***

Invited Speakers

***“Stuff: A Science Writer’s Wandering
Through the World of Materials”***

**Dr. Ivan Amato
Silver Spring, MD**

“Micro- and Nano-Layered Polymer Composites”

**Professor Eric Baer
Case Western Reserve University
Cleveland, OH**

“Theoretical Modeling of Polymers at Surfaces and Interfaces”

**Professor Anna Balazs
University of Pittsburgh
Pittsburgh, PA**

***“Mechanisms of Stereocontrol for Isotactic and Syndiotactic
Polymerizations of Olefins”***

**Professor John Bercaw
California Institute of Technology
Pasadena, CA**

“Surfaces Designed to Resist Marine Fouling”

**Dr. Robert Brady
Naval Research Laboratory
Washington, DC**

“The Significance of Single Site Metallocene Catalysis in New Polymer Technologies”

**Dr. Steve Chum
Dow Chemical Company
Freeport, TX**

“Interdiffusion of Reacting Thermosets into Thermoplastics”

**Professor John W. Gillespie, Jr.
University of Delaware
Newark, DE
and**

**Dr. Steven H. McKnight
Army Research Laboratory
Aberdeen, MD**

“Mesoscopic Pattern Formation in Multiphase Polymer Systems”

**Professor Takeji Hashimoto
Kyoto University
Kyoto, JAPAN**

“Damage Evolution, Fatigue & Creep Fracture of Polyethylene”

**Professor Anne Hiltner
Case Western Reserve University
Cleveland, OH**

“Molecular Design of Smart Surfaces”

**Professor Jeffrey Koberstein
University of Connecticut
Storrs, CT**

“Polymer-Polymer Interactions & Interfaces”

**Professor Donald R. Paul
University of Texas
Austin, TX**

“Design & Characterization of Fiber/Matrix Interphases for Composites”

**Professor Judy Riffle
Virginia Polytechnic Institute & State University
Blacksburg, VA**

“Biomimetic Design to Interphase Control in Complex Systems”

**Professor Mehmet Sarikaya
University of Washington
Seattle, WA**

“Self Organization of Supramolecular Materials”

**Professor Samuel Stupp
University of Illinois
Urbana, IL**

“Contact Mechanics Methods for Studying Interfacial Adhesion”

**Professor Matthew Tirrell
University of Minnesota
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Twenty-First Asilomar Conference
February 22-25, 1998

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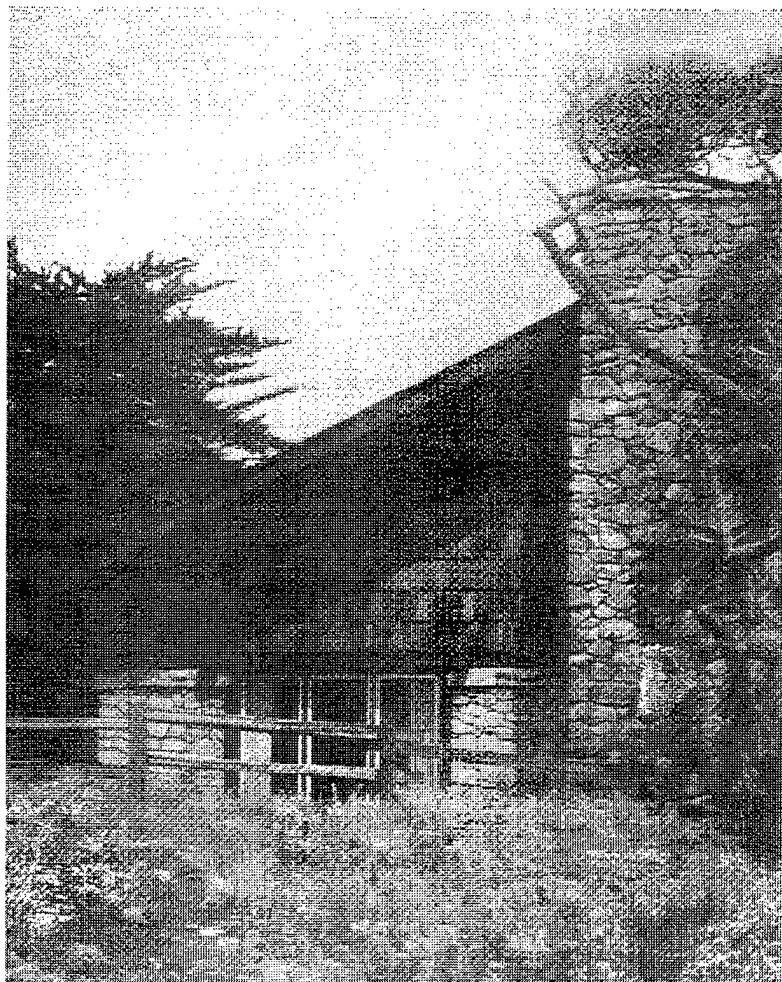
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Abstracts

Asilomar Conference



***Twenty-First Asilomar Conference
on Polymeric Materials***

February 22-25, 1998

Pacific Grove, CA

Ivan Amato

*Abstract for Talk at Asilomar Conference on Polymeric Materials
Pacific Grove, CA
February 22-25, 1998*

***Stuff: A Science Writer's Wanderings Through
the World of Materials***

From the moment we are born to the instant of our deaths (and even before and after those rather pivotal moments of our lives), we are in relentless, intimate contact with the stuff of the world. It might begin with a cotton swaddling cloth and end in a pine box, but it is stuff, stuff, stuff that we are relentlessly surrounded by. Nothing could be more obvious. And yet for most people, the materials of which absolutely every thing is made remain submerged below consciousness. They are in sight, yet out of mind. From time to time, everyone wakes up to the centrality of materials. This often happens when things go wrong, like when your wine glass falls from the table and shatters into a thousand pieces. That makes you think about glass. My entry to science writing served as my wake-up call to the material world, so much so, that I can no longer look at the world without thinking of the stuff it is made of. What's more, because of that alteration in the way I attend to things, the world has become infinitely more interesting. Since all the natural, synthetic, and high-and low-tech materials we know about now are but a tiny harbinger of the vast catalog of materials awaiting to be pulled from the Periodic Table's ultimate pantry of ingredients, there is a whole lot of stuff to look forward to.

Micro-and Nano-Layered Polymer Composites

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ABSTRACT

This lecture will emphasize the use of micro-and nano-layered polymer composites in the study of polymer-polymer interfacial phenomena. Four systems will be discussed (a) a miscible amorphous system, PC-Kodak; (b) a miscible crystalline system, HDPE-LLDPE; (c) an immiscible system, PC-SAN; and (d) a new three component immiscible system. Special emphasis will be on the kinetics of interdiffusion, and on the control and optimization of interfacial adhesion.

(a) The interdiffusion of two miscible polymers, polycarbonate (PC) and a copolyester (KO-DAR), was studied at temperatures from 200 to 230°C. The microlayer structure provided a large area of intimate contact between the two polymers with minimal mixing. Initially, two glass transition temperatures were observed by DSC that were intermediate between the glass transition temperatures of the pure components. Upon annealing, the glass transition temperatures shifted closer together, reflecting the extent to which interdiffusion had occurred. After no more than 2 hours of annealing, a single glass transition temperature was observed. A model was formulated based on Fick's law of diffusion that related the mutual diffusion coefficient, D , to the change in the glass transition temperatures. For the temperature range from 200 to 230°C, the value of D varied from 4.0×10^{-16} to 1.6×10^{-15} m²/s. The activation energy of interdiffusion was determined to be 95 kJ/mol.

(b) Kinetics of interdiffusion of a miscible crystallizable polymer pair, HDPE and LLDPE, was studied in order to characterize the conditions required to construct gradient morphologies from microlayers. Microlayers were taken into the melt for a period of time, and the compositional gradient was fixed by crystallization upon quenching. High specific interfacial area of microlayers offset the low diffusion mobility of

polymeric chains so that the microlayer system in the melt approached compositional homogeneity on a laboratory time scale. This specific pair of polymers with broad molecular weight distribution formed isomorphic blends upon crystallization from the melt. Thermal analysis of the quenched microlayered pair indicated systematic changes in the melting behavior with the composition gradient, which made it possible to quantify the progress of interdiffusion without chemical labeling. The thermograms were analyzed by applying a diffusion model formulated especially for a polydisperse system. The analysis revealed the role of different fractions, and allowed us to extract the diffusion coefficients for elementary chains in the developing melt blend from the net kinetics of interdiffusion. It was confirmed that the molecular weight dependence of the polyethylene chain diffusion coefficient follows reptation theory. The magnitudes of the diffusion coefficients and activation energy were found to correlate well with data of previous studies on monodisperse polyethylene species.

(c) The peel strength and delamination failure mode of coextruded microlayer sheet consisting of alternating layers of polycarbonate (PC) and poly(styrene-co-acrylonitrile) (SAN) were studied with the T-peel test. Four delamination modes were observed: two modes where the crack propagated along the PC-SAN interface, and two other modes where the crack propagated through crazes in the SAN. The SAN layer thickness determined whether crack propagation was interfacial or through crazes. Experiments were carried out on microlayers with thin SAN layers, to ensure that delamination would occur predominantly by an interfacial mechanism, and with PC layers that were thick enough to prevent the delamination crack from tearing through the PC. A broad maximum in the interfacial toughness occurred at about 20% AN. When microlayers with thicker SAN layers were tested, crazing in SAN's with 15-25% AN increased the delamination toughness and greatly exaggerated the maximum at 20% AN. Crazing only occurred if the interfacial toughness of PC-SAN exceeded the SAN crazing condition. When the critical condition for SAN crazing, which increased linearly with AN content, was overlayed with the interfacial toughness curve, transitions in the failure mode were correctly predicted where the craze line crossed the interfacial failure curve.

Theoretical Modeling of Polymers at Surfaces and Interfaces

Anna C. Balazs

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Polymer-clay nanocomposites constitute a new class of materials where nano-scale clay particles are dispersed within a polymer matrix. Such composites exhibit dramatic increases in tensile strength, heat resistance, and decreases in gas permeability when compared to the pure polymer matrix. The thermodynamic stability of the composite depends on the molecular interactions between the polymers and the surface of the clay particles. To model the phase behavior of the composite, we recently modified the Onsager model for the liquid crystalline behavior of rigid rods. Instead of rods, we considered discs, whose diameter is given by D and whose width is L . To the Onsager model, we added a Flory-Huggins term, which describes the translational entropy of the polymers and the energetic interaction between the polymers and the discs. We derive an energy expression for the system; by minimizing this free energy and calculating the chemical potentials, we construct phase diagrams for the polymer/disc and polymer/solvent/disc mixtures. The findings provide guidelines for tailoring the interaction energies, the polymer molecular weight and the volume fraction of the different components to fabricate thermodynamically stable mixtures with the desired morphology.

Mechanisms of Stereocontrol in Isotactic and Syndiotactic Polymerizations of Olefins

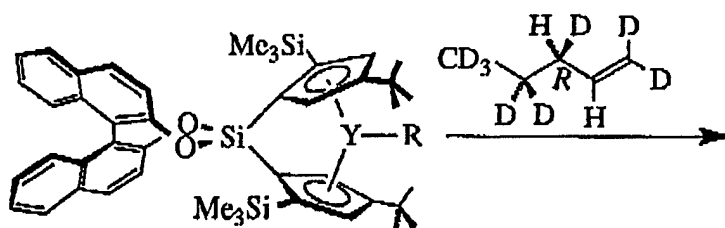
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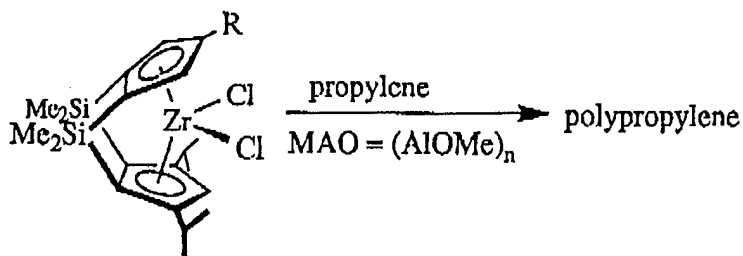
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Single component ytrocene catalysts have been prepared in enantiopure form (below) for the purpose of investigating the mechanism of stereoselective chain growth for isotactic Ziegler/Natta α -olefin polymerizations. Isotope effects and stereochemical probes have been used to define the transition state structure for 1-pentene insertion into yttrium-hydrogen and yttrium-pentyl bonds. The findings have identified the most important interactions that stereodifferentiate between the enantiofaces of α olefins in chain propagation.¹



Basing our design on the transition structure for isospecific catalysts, we have developed a new class of metallocene catalysts (below) capable of producing highly syndiotactic polypropylene (PP) ($R = \text{CHMe}_2$) or an "ambi-specific" catalyst ($R = \text{CHMeCMe}_3$) that produces moderately syndiotactic PP at high propylene concentration, switching to moderately isospecific at low propylene concentration.² At intermediate concentrations of propylene a polypropylene resembling hemi-isotactic is obtained. The mechanisms for these stereospecific polymerizations have been studied.



1. Gilchrist, J. H.; Bercaw, J. E. *J. Am. Chem. Soc.* **1996**, *118*, 12021.
2. Herzog, T. A.; Zubris, D. L.; Bercaw, J. E. *J. Am. Chem. Soc.* **1996**, *118*, 11988.

Surfaces Designed to Resist Marine Fouling

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Our research strives to construct and understand polymer surfaces with no inherent power to interact with other materials, especially with the biological polymers used by marine organisms to bind themselves to objects in the sea. We limit ourselves to organic coating technologies which conform to environmental and worker safety regulations and are suitable to industrial applications. During the past 15 years we have synthesized polymers, formulated them into coatings, and measured the resistance of the coatings to marine fouling in the United States (Florida, Maryland, Hawaii), Australia, and Canada. We have found, as have many other research groups, that the polymer surface property which most frequently correlates with resistance to bioadhesion is the critical surface tension (γ_c); in fact, a generalized relationship between the γ_c of the polymer surface and the relative amount of bioadhesion has been known for more than twenty years.

However, this relationship is also influenced by other bulk and surface properties of the polymer. In this presentation we will discuss several alternative interpretations of the relationship between γ_c and bioadhesion, and develop insights into the requirements for the structure and dynamics of polymers which refuse or resist strong bonds to other materials.

We will also present portions of our past and present work on polymer synthesis, coatings formulation, and testing of coatings in oceans around the world. We have focused on fluorinated polymers and polysiloxane polymers because each possesses a lower critical surface tension. The two classes of polymers differ substantially in their performance, and this performance will be interpreted in terms of the requirements developed in the first portion of the presentation. Frequently these coatings adhere to the substrate equally as poorly as biofouling adheres to them. This and other practical polymer-related issues will also be discussed.

The Significance of Single Site Metallocene Catalysis in New Polymer Technologies

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Abstract

The use of metallocene and single site catalyst technology has allowed a very rapid development of new olefin copolymers with a wide range of structure and related properties. This technology has initiated a major revolution for the polyolefin industry. Several new families of metallocene/single site catalyst based olefin copolymers, including polyolefin elastomers (e.g., Engage™), polyolefin plastomers (e.g., Affinity™; Exact™), EPDM, enhanced PE (e.g., Elite™, Exceed™), polypropylenes and ethylene/styrene interpolymers (ESI) have been commercialized and/or under major commercial development in the 1990's. In addition to these commercial activities, several other single site catalyst related technologies that allow the co-polymerization of alpha olefins with polar comonomers are also under industrial and academic development in the recent year.

The major advantage of metallocene and single site catalysts is its versatility in building polymer structures with well defined molecular structures. This capability allows the plastics industries to tailor design new polymers using molecular architecture approaches. Polymer producers who can leverage the catalyst and process technologies with product design, performance requirements and materials science know-how to deliver differentiated products to their customers with speed will continue to lead this significant industry revolution into the next century.

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HOLLOW CYLINDER, CORE-SHELL MORPHOLOGY IN BLENDS OF DIBLOCK COPOLYMERS AND HOMOPOLYMER

Samuel P. Gido
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The morphology of blends of poly(styrene-*b*-cyclohexadiene) diblock copolymer with about 20 weight percent homopolystyrene were investigated using transmission electron microscopy (TEM), small angle X-ray scattering (SAXS), and small angle neutron Scattering (SANS). TEM micrographs clearly show a hexagonal lattice of polycyclohexadiene (PCHD) cylindrical annuli in a polystyrene (PS) matrix. There is an additional PS microdomain in the core of each PCHD cylinder. The thermodynamics of this hollow cylinder morphology was analyzed as a two component phase separation with two independent variables, homopolystyrene concentration and curvature of the interface between PS and PCHD domains. The system phase separates into an inner core with an interface curved toward the PS domain and an outer shell with the interface curved away from the PS matrix.

Diffusion of Reacting Thermosets into Thermoplastic Polymers

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Professor John W. Gillespie, Jr
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Abstract

Research at our laboratories has shown that adhesion between thermoplastic polymers and cross-linking thermoset resins can be dramatically improved in cases where diffusion of the thermosetting pre-polymers into the thermoplastic is possible. Joint toughness under quasi-static and dynamic loading has been shown to be directly related to the size of the diffuse interphase. The graded interphase that is formed is believed to enhance practical bond strength through entanglements between the thermoplastic polymer chains and the network structure of the curing adhesive. Our present research has focused on studying the fundamental aspects of the diffusion process in order to provide predictive process models that can be used to optimize bond properties. Towards this end, we have studied the diffusion of a diglycidyl ether of bisphenol A (DGEBA) epoxy and an aliphatic diamine, bis (p-aminocyclohexyl) methane (PACM 20) into compatible thermoplastic polymers including polysulfone (PSU) and polyetheretherketone (PEEK). First, the diffusivity of each single component into the thermoplastic films was quantified using a novel ATR-FTIR spectroscopic technique at several temperatures. Not surprisingly, these studies revealed that the smaller amine will diffuse faster than epoxy at a given temperature. Also, the epoxy demonstrated Fickian diffusion behavior, while the amine exhibited slight deviations from ideal Fickian behavior, which were attributed to suspected polysulfone swelling. Next, we examined the simultaneous diffusion and reaction of the two component thermosetting system into thermoplastic polymers. Results indicated that the diffusion of the larger epoxy molecule in polysulfone occurred more quickly when diffusing in the presence of the amine due to swelling of the polysulfone film. This effect was further quantified by evaluating the diffusion of a model non-reactive DGEBA type molecule in amine-saturated PSU. We have also developed analytical and numerical models which incorporate diffusion and reaction kinetics to predict diffusion into amorphous and semi-crystalline thermoplastic polymers. The models have been experimentally validated by examination of the diffuse interphase using electron microscopy, electron dispersive spectroscopy, atomic force microscopy, and ATR-FTIR. The interphase thickness was observed to range from 1 to 15 micrometers depending on processing conditions. Additionally, SEM examination of the interphase revealed a microstructure consistent with PSU/ epoxy-amine interpenetrating networks. Subsequent mechanical testing of bonded joint demonstrated a direct relationship between fracture toughness and interphase thickness. This work demonstrates the possibility of designing adhesive interphases to achieve optimum performance through control of materials and processing parameters.

Mesoscopic Pattern Formation in Multiphase
Polymer Systems: Sponge-like Structures in Phase-separating Polymers.

by

Takeji Hashimoto

Department of Polymer Chemistry, Graduate School of Engineering,
Kyoto University, and Hashimoto Polymer Phasing Project, ERATO, JST

We will discuss a very fundamental aspect of phase-separating polymer systems. We focuss on real-space analysis of the phase-separating structures in the late stage spinodal decomposition of symmetric and isometric polymer mixtures. We found that the 3 dimensional structure of the systems constructed with a laser scanning confocal microscopy has characteristics of "sponge-like" structure. This sponge-like structure can be predicted by a general, nonlinear time-evolution equation called the time-dependent Ginzburg-Landau equation. We found this structure is rather universal, applicable to critical mixtures of simple liquids, metallic alloys in the late stage spinodal decomposition and equilibrium microemulsion (oil/water/ surfactant) systems at hydrophile-lypophile balance. We have also developed algorithms to determine area-averaged mean $\langle H \rangle$ and Gaussian curvatures $\langle K \rangle$ for the interfaces and their distributions from the values $\langle H \rangle$ and $\langle K \rangle$ based on principles of differential geometry and found $\langle H \rangle \cong 0$ and $\langle K \rangle < 0$ (interfaces being composed of saddles somewhat similar to a minimal surface, though not equal rigorously speaking) throughout the spinodal decomposition process.

Damage Evolution, Fatigue & Creep Fracture of Polyethylene

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Abstract

Step-wise fatigue crack propagation was studied in a range of polyethylene resins, some of which are candidates for use in pipes for natural gas distribution. Examination of the effect of molding conditions on fatigue crack propagation in a pipe resin indicated that fast-cooling under pressure produced specimens with the same crack resistance as specimens taken from extruded pipe. The mechanism of step-wise crack propagation in fatigue was the same as reported previously for creep loading. Observations of the region ahead of the arrested crack revealed a complex damage zone that consisted of a thick membrane at the crack tip followed by a main craze with subsidiary shear crazes that emerged from the crack tip at an angle to the main craze. The effects of molecular parameters, such as molecular weight, comonomer content and branch distribution, on the kinetics of fatigue crack propagation were examined. Correlation of creep and fatigue crack resistance made it possible to relate fatigue fracture toughness to molecular parameters by invoking concepts of craze fibril stability developed for creep.

Molecular Design of Smart Surfaces

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A new concept for polymer surface modification is described that employs surface-active ω -functional block copolymers as additives to create polymers with smart surfaces. The block copolymers are composed of three components: a low surface energy block that causes the copolymer to segregate to the surface of the matrix homopolymer to which it is added, an anchor block that tethers the copolymer into that matrix, and a functional group located at the terminus of the surface-active block. The functional end group is selected to interact selectively with a complementary receptor on the target substrate. When the modified polymer surface and a substrate are placed in contact, adhesion is enhanced only if the functional end group senses an appropriate receptor on that substrate with which it can form the specific interaction. If a receptor is not present, the modified surface exhibits release properties. This class of copolymer additives can thereby be employed to create smart polymer surfaces with selective adhesive properties.

We present preliminary results that demonstrate how this new concept can be employed to modify the surface of polystyrene (PS) and impart selective adhesion toward either poly(methyl methacrylate) (PMMA) or poly(dimethylsiloxane) (PDMS) substrates. In the latter case, an ω -silane functional poly(styrene-*b*-dimethylsiloxane) copolymer is adsorbed at the PS surface. When contacted with a PDMS gel, a covalent bond is formed by hydrosilylation with residual vinyl groups in the gel and the interface is bridged, as shown in the figure below. This same block copolymer gives release properties toward PMMA, demonstrating how selective adhesion properties may be imparted through the use of surface-active ω -functional block copolymers.

ADVANCES IN ATOMIC FORCE MICROSCOPY OF POLYMERS

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In recent years a family of microscopic techniques, which are applied for studies of polymer materials, has included atomic force microscopy (AFM). Recent results obtained in AFM studies of various polymer samples will be presented in the report. They demonstrate the unique capabilities of AFM in high-resolution imaging of polymer morphology, and in visualization of sample composition in heterogeneous samples. High resolution imaging of polymer chains and their conformational order has been achieved in contact mode AFM. However, imaging of soft polymers in the contact mode may be destructive due to strong tip-sample force interactions leading to shear deformation. This difficulty has been overcome after the tapping mode was introduced. It is characterized by negligible lateral forces and by a short time of the tip-sample contact that essentially reduced sample damage. At present, this mode offers a broad range of applications. For high-resolution imaging of non-periodic surfaces, where the resolution is determined by the tip-sample contact area, the minimization of the tip-force is needed. It has been shown that a lateral resolution of 2-3 nm can be achieved on polymer samples. This, in combination with high sensitivity to surface corrugations, makes AFM an indispensable method for examining morphology and nanostructure of polymers. The ability to control and to vary the tip-force allows one to examine local adhesive and mechanical properties and use them for mapping sample composition in heterogeneous samples. The phase difference of the free-oscillating probe and the probe interacting with a sample describes the level of the force interactions and the energy dissipating in the tip-sample junction. Monitoring of the phase changes helps to optimize experimental parameters for low-force imaging (*light* tapping) or for imaging at elevated forces (*hard* tapping), where the energy dissipation is maximal. In *light* tapping, the height images are most close to true surface topography, whereas the phase images are generally featureless. At high-force imaging of heterogeneous samples, the phase variations are related to the differences of the energy dissipated on different components. Though several tip-sample interactions contribute to the dissipation, however, differences in mechanical properties of components are responsible for the phase contrast in *hard* tapping. The experiments conducted at such conditions on a number of polymer samples show high sensitivity of the phase contrast to sample composition.

CONTROLLED ARCHITECTURE GRAFT COPOLYMERS BY ANIONIC POLYMERIZATION

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Abstract

The synthesis and characterization of well-defined poly(isoprene-graft-styrene)s will be described. Through the use of living anionic polymerization and controlled chlorosilane linking chemistry, we have been able to achieve an unprecedented level of control over branch number and branch placement in graft copolymers. Procedures for making materials with single branches at predetermined sites along the polymer backbone ("simple grafts"), Pi and H architectures ("double grafts"), and graft copolymers with regularly-placed multiple trifunctional and tetrafunctional branch points ("centipedes") will be presented. We will also briefly discuss the influence of macromolecular architecture on block copolymer morphology.

Polymer-Polymer Interactions and Interfaces

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Abstract

Interfacial characteristics define certain aspects of the behavior of multiphase polymer blends or composites. The nature of the polymer-polymer interface, e.g., interfacial tension and thickness, is quantitatively linked to the polymer-polymer interaction energy (as defined in thermodynamic theories of mixing) as first revealed in the theory of Helfand. The purpose of this study is to compare experimentally measured interfacial characteristics (e.g. interface thickness determined by neutron reflection experiments) with those predicted by theory using separately determined interaction energies assessed by experimental phase behavior observations and interpreted by various theories. Typically the interaction energies between repeat unit pairs can be evaluated by noting miscibility-immiscibility boundaries that result from changes in temperature, molecular weight, or copolymer composition. For copolymers the polymer-polymer interaction energies are expressed in terms of interactions between repeat unit pairs using a mean-field binary interaction model. Systems being considered include bisphenol-A polycarbonate, PC, or poly(2,6-dimethyl-1,4-phenylene oxide), PPO, with copolymers of styrene and acrylonitrile, SAN, or maleic anhydride, SMA.

The Effect of Different Types of Rubber on Impact Resistance of Polyamide 6 and Polyamide 66

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Abstract

The toughening enhancement of Polyamide 6 and Polyamide 66 modified with two different types of rubber was evaluated. The processing conditions, blends morphology and the nature of rubber were taken as key parameters in order to understand the final properties of blends. More specifically, a correlation between the observed impact level as measured on notched Izod samples; rubber particle size distribution and viscoelastic behaviour of rubbers has been found. The particle size distribution seems to prevail over all others parameters affecting impact enhancement when Impact tests were carried out at room temperature; unlike, at low temperatures, the nature of rubbers become very important. The softer the rubber, the better the Impact.

In addition, the fact that Polyamide 66 is more reactive towards this kind of modifiers was confirmed.

Design and Characterization of Fiber/Matrix Interphases for Composites

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Fiber reinforced polymer matrix composites are finding increased use in construction, infrastructure, and ground transportation applications where long term durability (mechanical and environmental) is a key issue (1). This has prompted impetus for fundamental studies of the relationships between the fiber/matrix "interphase" region and composite durability in both our laboratories and those of others (2). A comparison of static and dynamic performance with a basic set of polymeric interphases exhibiting brittle, tough and elastomeric properties for carbon fiber/vinyl ester composites is being conducted. A number of techniques are being used to evaluate both the "macro and micro" properties of the composites as a function of interphase structure. These include transmission electron microscopy, atomic force microscopy, and nano-indentation to map chemical compositions and mechanical properties across bi-layer films comprised of the fiber "sizings" and the vinyl ester matrices. Microdebond tests have been carried out by the Korean group to probe adhesion between the "sized" fibers and matrices. Fatigue cycling has proven to be particularly useful in highlighting the influence of the tailored interphases on the durability of the carbon fiber/vinyl ester composites.

Composite fatigue properties of AS-4/vinyl ester composites having a tough, ductile polyhydroxyether thermoplastic in the "interphase" region can be improved dramatically (relative to using unsized fibers) with as little as ≈ 1 wt. % of the sizing in the composite. The thermoplastic sizing is soluble in the thermosetting resin prior to cure, but microphase separates into discrete domains during matrix curing. A gradient in chemical composition and morphology results in moving outward from the fiber into the thermoset matrix. It is hypothesized that the unusually good fatigue resistance of composites from these materials can be at least partially attributed to this interphase gradient.

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BIOMIMETIC DESIGN TO INTERPHASE CONTROL IN COMPLEX SYSTEMS

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Structural control of inorganic materials at the nanoscale is a key to the synthesis of materials with new and improved physical properties in applications including nanotechnology, smart materials, and quantum structures. Biological hard tissues may serve as models for novel engineered materials as biocomposites have excellent combination of physical properties that are related to their highly ordered hierarchical structures. The intricate nano- and micro-architecture of biocomposites (bone, dentin, bacterial particles, mollusc shells) are controlled at the molecular level at interphases by macromolecules through interactions with mineral phases. In this presentation, specific hard tissues (mollusc shells, bacterial particles, and dental tissues) will be discussed as biocomposite example that offer materials science and engineering lessons for architected complex materials.

The central issue, *mimicking of biological structures*, requires the use of proteins that have affinity to inorganic surfaces. Although proteins can be isolated from biological tissues, a more practical strategy is to use genetic engineering techniques to develop novel none-natural proteins with high affinity to inorganic surfaces. The second part of the presentation will discuss *combinatorial genetic* techniques that permit isolation of specific recognition elements for inorganic surfaces, including those not realized by natural proteins, in the absence of *apriori* prediction of necessary structures. The results could have significant implications in tailoring formation and assembly of ordered structures of metals, functional ceramics, semiconductors, and ferroelectrics in nanotechnology and biomimetics.

SELF ORGANIZATION OF SUPRAMOLECULAR MATERIALS

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ABSTRACT

An interesting target in polymer science is to find pathways to supramolecular units with regular shapes and molar masses in the range of those associated with macromolecules. These shape invariant units, analogous to folded proteins, could offer a very exciting toolbox for the rational design of highly functional materials. We are pursuing access to these polymers with designed molecules programmed to self assemble into supramolecular nanostructures. These nanostructures at a post-assembly stage can be converted to shaped covalent polymers following nanoscopic polymerizations. Space filling requirements for shape invariant nanostructures, and the great structural diversity that can be achieved by molecular synthesis, can lead to novel materials with unique potential to be multifunctional and easily processable. This lecture will describe the recent discovery of specific systems in which the precursor molecules were designed targeting specific physical properties. Our original system demonstrated self organization into tape-like materials with chemically dissimilar surfaces. As such these materials could fulfill functions ranging for corrosion protection barriers for metals to self organizing icephobic coatings. Given their noncentrosymmetric character these self organizing thin films naturally integrate other properties such as nonlinear optical response and even piezoelectricity.

Based on principles identified before, we designed very recently novel molecules containing photoluminescent blocks, ion-conducting blocks, and electron donor blocks. These electron donor blocks were designed to also activate repulsive forces upon self assembly in order to limit the growth of nanostructures. Interestingly, we discovered these highly functional triblock structures self assembled into discrete aggregates and ordered at larger length scales into superlattices and polar layered structures. These organizational features plus their electronic and photonic capabilities could transform them into highly multifunctional materials by self assembly. The thick 3D arrays of nanostructures they form, equivalent to thousands of molecular layers, may also allow us to control the wavelength of light emitted as well as quantum efficiency. In other examples to be discussed in the lecture, we have begun to develop strategies to create nanostructures with cavities that may serve to sense chemicals or molecular objects in the environment.

CONTACT MECHANICS METHOD FOR STUDYING INTERFACIAL MATERIALS

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Contact mechanics is the study of the deformation of solid bodies in contact under load. It is becoming increasingly useful in the study of polymer adhesion, particularly in a near-static, low-rate regime where the separability of surface energy and rheological effects is most accessible. In some ways, contact mechanics for solids plays a role similar to contact angle measurement for liquids. Examples of the application of contact mechanics to problems of glassy polymers, viscoelastic copolymers and surfaces treated with amphiphilic molecules will be discussed. The viscoelastic problem will be treated in depth.

We have measured the surface energies of several viscoelastic polymers, using contact mechanics methods. The materials studied were diblock copolymers of poly(ethylene)-poly(ethylene-propylene) (PE-PEP) having different PE volume fractions and molecular weights. The materials exhibit differing viscoelastic relaxation functions in the bulk. Surface energies were determined from contact mechanics experiments in the loading mode, analyzed by incorporating the bulk viscoelastic effects into the Johnson-Kendall-Roberts theory of adhesive elastic contacts. The samples were made of spherical caps of the materials formed by first melting, and then cooling to room temperature. The measured values of the surface energies are close to the reported value for that of the surface-active PEP block, based on prior contact angle measurements, indicating that reliable surface energy values can be extracted from contact mechanics experiments, suitably analyzed to account for viscoelastic behavior. We believe that this method may be generalizable to surface and interfacial energy studies of a wide range of viscoelastic polymers.